By very large oxygen quantities, the catalyst is fully poisoned. Various possible explanations are given for this fact (Ref 8). Figure 4 shows the temperature effect on the molecular weight of the polymer at an optimum oxygen content in propylene. At a temperature increase from 30 to 80°, the yield decreases linearly as expected. The stereospecific polymerization processes can apparently be realized by any known initiation mechanism. The process can be imagined according to the ion- or radical mechanism. The stereospecificity in the respective class of catalysts is only determined by the degree of orderliness of the catalytic surface. The authors think that a radical mechanism is not impossible in polymerization with Tsigler catalysts (for the first time in Ref 4). The said catalyst has, however, not a high stereospecificity in the reactions of propylene polymerization. There are 4 figures and 11 references, 2 of which are Soviet.

SUBMITTED: April 22, 1959

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AUTHORS: Krentsel', B. A., Topchiyev, A. V., Academician, Il'ina, D. Ye. SOV/20-128-6-26/63

TITLE: Chlorination of Monochloropropanes

PERIODICAL: Doklady Akademii nauk SSSR, 1959, Vol 128, Nr 6, pp 1192 - 1195 (USSR)

ABSTRACT: The sequence of substitution of hydrogen atoms by chlorine in the chlorination of monochlorine-substituted compounds to dichlorides is of high interest for understanding the influence of the molecular structure of a paraffin on the rules of its chlorination. The opinions of several investigators disagree in this respect (Refs 1-7). According to reference 8, the temperature of chlorination has a certain influence on the ratio of isomeric dichlorides. Hence, it appears that, contrary to the rules found by H. B. Hass and E. T. McBee (Refs 1,2), not only the formation of 1,1- but also of 1,1,1-chlorine-substituted chlorides is possible. D. V. Tishchenko and A. Churbakov (Ref 9) also consider probable the formation of the former from monochlorides. The results of thermal chlorination of isomeric chloropropanes are listed in table 1. The latter shows that only 1,1-, 1,2-, and 1,3-dichloropropanes develop. The absence of

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Chlorination of Monochloropropanes

2,2-dichloropropane suggests that no pyrolysis occurs under the given conditions. On the other hand, a considerable quantity of 2,2-dichloropropane and a somewhat smaller quantity of 1,2-substituted compounds are formed in the thermal chlorination of 2-chloropropane. The results obtained once more confirm the formation of $\alpha\alpha'$-substituted compounds in the chlorination of chloroalkanes. Further, the photochemical chlorination of chloropropanes was studied. The authors tried here to avoid the formation of 3- and polychlorides. Table 3 shows the results. The curves of fractionated distillation are shown in figures 1 and 2. Table 4 shows the average isomer composition of the dichloropropanes produced. Thus, the position of the chlorine atom in chloroalkane has a considerable influence on the sequence of the further substitution of hydrogen by chlorine. In the case of 2-chloropropane, the principal chlorine quantity substitutes the hydrogen on the C-atom which is already bound to chlorine. 2,2-dichloropropane is mainly formed. If, however, 1-chloropropane is chlorinated, the substitution proceeds in such a way that 1,2-dichloropropane is formed. This is explained by the difference in the electronic structure of the isomeric alkyl chlorides. [redacted]

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SOV/20-129-4-23/68

AUTHORS: Ivanova, T. I., Krentsel', B. A., Pokatilo, N. A., Topchiyev, A. V., Academician

TITLE: Polymerization of 3-Methyl Butene-1

PERIODICAL: Doklady Akademii nauk SSSR, 1959, Vol 129, Nr 4, pp 799-800 (USSR)

ABSTRACT: The authors investigated the polymerization of 3-methyl butene-1 with a complex organometallic catalyst. 3-methyl butene-1 was obtained by pyrolysis of isoamyl acetate in a yield of 97%. The dependences observed in the pyrolysis are graphically represented in figures 1 and 2. $Al(C_2H_5)_3$ or $Al(i\text{-}C_4H_9)_3$ and $TiCl_4$ or $TiCl_3$ were used as catalyst components. $Al(C_2H_5)_3$ and $Al(i\text{-}C_4H_9)_3$ were dissolved in benzene before they were used. The reaction mentioned in the title was made in carefully purified and dried heptane and in argon atmosphere. The obtained poly-3-methyl butene-1 is a white powder (melting point approximately at 240°). The properties and the polymer constants are determined. The content of the isotactic component was determined by successive extraction with boiling ether and heptane (similar to the investigation of

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polypropylene). Some samples were investigated by radiographic methods (Fig 3). Some characteristic experiments (Nr 10 and 27) are described. The low content of the isotactic component results from the use of $Al(i\text{-}C_4H_9)_3$ and from the impurification of the $TiCl_3$ surface by NaCl. There are 3 figures.

SUBMITTED: July 16, 1959

KRENTSEL, B. A.

PHASE I BOOK EXPLOITATION SOV/4984

International symposium on macromolecular chemistry. Moscow, 1960.

Mezhdunarodnyy simpozium po makromolekulyarnoy khimii SSSR, Moskva, 14-18 iyunya 1960 g.; doklady i avtoreferaty. Sektsiya III. (International Symposium on Macromolecular Chemistry Held in Moscow, June 14-18, 1960; Papers and Summaries) Section III. [Moscow, Izd-vo AN SSSR, 1960] 469 p. 55,000 copies printed.

Tech. Ed.: P. S. Kashina.

Sponsoring Agency: The International Union of Pure and Applied Chemistry. Commission on Macromolecular Chemistry.

PURPOSE: This book is intended for chemists interested in polymerization reactions and the synthesis of high molecular compounds.

COVERAGE: This is Section III of a multivolume work containing papers on macromolecular chemistry. The articles in general deal with the kinetics of polymerization reactions, the synthesis of special-purpose polymers, e.g., ion exchange resins, semiconductor materials, etc., methods of catalyzing polymerization reactions, properties and chemical interactions of high molecular materials, and the effects of various factors on polymerization and the degradation of high molecular compounds. No personalities are mentioned. References given follow the articles.

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APPROVED FOR RELEASE: Monday, July 31, 2000 CIA-RDP86-00513R000826410(

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E202/E192

5.3833

AUTHORS: Topchiyev, A.V., Tolchinskiy, I.M., Krentsel', B.A., and Smolyan, Z.S.

TITLE: Polymerization of olefines in the preparation of semi-products for plastics and synthetic fibres

PERIODICAL: Referativnyy zhurnal, Khimiya, no.11, 1962, 586-587, abstract 11 P32. (Tr. Vses. soveshchaniya po khim. pererabotke neft. uglevodorodov v poluprodukty dlya sinteza volokon i plast. mass. ("Proceedings of the All-Union Conference on the Chemical Conversion of Petroleum Hydrocarbons to Half-finished Products for the Synthesis of Fibres and Plastics"), Baku, AN Azerb.SSR, 1960, 37-39).

TEXT: Synthesis of polypropylene (PP) with catalyst (KT) $Al(C_2H_5)_3$ (20% solution in kerosene) together with $TiCl_4$. $Al(C_2H_5)_3$, received by direct synthesis and from ethyl bromide, was studied. Propylene was prepared by dehydration of isopropanol (99.2% C_3H_6 and 0.8% $N_2 + O_2$). Propylene-propane

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fraction of the petroleum gas (85.1% C_3H_6) was also used. PP was synthesized in a reactor with a stirrer and reflux condenser; the reactor being filled first with the solvent (benzene "Kalosha") and the necessary quantity of catalyst. Next, propylene free from contaminants was introduced. Upon completion of the reaction the reactor was cooled down to +10 °C and the contents were worked by mixing with absolute methyl alcohol in order to decompose the residual catalyst. PP was filtered off and repeatedly washed with methyl alcohol and water, then it was dried at 60-70 °C until constant weight. The effects of pressure, temperature, catalyst concentration, molar ratio of $Al(C_2H_5)_3$ to $TiCl_4$ on the yield and composition of the polymer obtained were studied. It was found that at atmospheric as well as at increased (4-6 atg) pressures, the best results were obtained at temperatures $\leq$ 50 °C. The work with pure propylene and commercial propane-propylene fraction gave substantially the same results. X-ray diffraction photograph, infrared spectrum

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and temperatures of melting of the obtained polymers showed the presence of 75% crystalline phase. The possibility of using a mixture of $Al(C_2H_5)_3$ and $Al(C_2H_5)_2Br$, and also $Al(iso\text{-}C_4H_9)_3$ mixed with $TiCl_4$ as a catalyst was also studied.

[Abstractor's note: Complete translation.]

Card 3/3

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S/063/60/005/005/003/021
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AUTHORS: Kargin, V.A., Academician, Topchiyev, A.V., Academician, Krentsel', B.A., Doctor of Chemical Sciences, Polak, L.S., Doctor of Physico-Mathematical Sciences, Davydov, B.E., Candidate of Chemical Sciences

TITLE: Semiconductor Properties of Polymer Materials

PERIODICAL: Zhurnal Vsesoyuznogo Khimicheskogo Obshchestva im. D.I. Mendeleyeva, 1960, No. 5, Vol. 5, pp. 507-514

TEXT: The authors deal with the problems of developing new classes of polymers with certain predetermined electrophysical properties necessary for industry, particularly semiconductivity. These problems have been one of the main subjects of scientific research in the physics and chemistry of polymers. An analysis of published works on the conductivity of low-molecular organic compounds has shown that their semiconductivity properties are connected with the π-electrons of the conjugated bonds in aliphatic chains

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Semiconductor Properties of Polymer Materials

or rings. "Metal-likeness" is said to be the result of a collection of the π-electrons in a conjugated system, and from this stand-point the polymer macromolecules with conjugated double bonds are of particular interest in the production of materials having special electrophysical properties, including that of semiconductivity. A list of available data is presented on ordinary semiconductors comparing them to the structures and chemical features of polymers. Semiconductors are characterized by the electroconductivity values of 10^{-8}-10 $ohm^{-1} \cdot cm^{-1}$, increasing with an increase in temperature, and a concentration of the charge carriers of about 10^{10}-10^{21} electrons or electronic "holes" in a cm^3. It is pointed out that deviations from stoichiometry or any irregularity of the chain of the macromolecules' main valencies can have the same effect as admixtures in polymers on their semiconductivity properties. The distance between neighboring energy levels being about 10^{-22} ev, the sum total of these is regarded as a compact band about 1 ev wide and the energy value of the electron can be anywhere within this range. This band of energy states is called a zone. For all solid

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bodies, i.e., metals, semiconductors and dielectrics, the lower zone of electronic levels is the wide, so-called valency zone of the electrons fastened to certain atoms. A difference is noted between the listed three types of solid bodies when there is a shift to a higher energy level. Semiconductors having no additional levels in the forbidden zone are called semiconductors with self-conductivity. In the presence of an electrical field the free electrons and "holes" are the charge carriers. It is pointed out that real bodies always contain admixtures, creating admixture levels in the forbidden zone of the semiconductor located either closer to the upper or lower zone, in both cases causing the occurrence of additional admixture conductivity. The admixtures are called donor type in the first case and acceptor type in the second. It is assumed that any irregularity of the cromolecules usually creates acceptor admixtures. The mobility of the charge carriers is said to depend on the temperature and concentration of the admixtures and to decrease with an increase in the temperature and amount of admixture. Special interest is shown in the semiconductor type discovered by de Boer (Ref. 3), where part of the atoms of the lattice is replaced by atoms with almost the same size but a difference in valency. The method by which they are produced was developed for oxide semiconductors,

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and consists in adding metals to the sample having a valency differing by a unit of 1 from the valency of the main metal. It is thought possible to form new synthetic polymers having semiconductor properties by a similar method of introducing metals into the chain of the macromolecule. Ordinary polymers have a certain amount of electroconductivity (Ref. 4,5), which depends on the temperature, and is expressed by $\sigma \sim \exp -\frac{E}{kT}$, where E is a certain activation energy, T the absolute temperature, k Boltzmann's constant. From this relationship the authors have attempted to solve the problem of establishing the connection between the polymer's structure and its electrophysical or electroconductivity properties. In solving this problem they based their analysis on the known aspects of the electroconductivity of low-molecular (including organic) compounds. This was followed by the determination of the characteristic features of the polymer structure. The problem of electroconductivity in organic polymers was divided into two parts: 1) the movement of electrons in the macromolecule, 2) transfer of electrons (or holes) from molecule to molecule. In the first part, an isolated linear macromolecule with the same bonds is analyzed:

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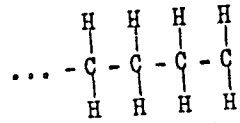

. The exact path followed by the potential of the electrical field formed by the electrons and nuclei of this type of system is not known, but the field changes periodically in space, and its period is determined by the periodicity of the molecular chain structure. An electron is theoretically placed into this field and its movement is regarded through the Schroedinger equation for an electron in a periodic field, the solution of which in this case is said to be the wave functions according to Block (Ref. 6): $\Psi = \varphi_\eta e^{i\cdot h\cdot x}$, where $\varphi_\eta(x)$ is a function depending on the wave number η, and is periodic relative to x; the magnitude of the period is determined by the structure of the molecule: by the length of the interatomic bonds, etc. This solution causes a zonal structure (Ref. 4,5). In calculating these fields the authors state that the theory of disturbance of quantum mechanics is used analyzing two extreme cases: a) a strong bond, b) a weak bond. It is pointed out that a real macromolecule can have conductivity if there are electrons in it whith sufficient probability of shift under the effect of an external electrical field with its component along

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the molecular chain. The authors draw the conclusion that the probable necessary condition for the existence of electroconductivity in a macromolecule is the presence of multiple, particularly double bonds. It is considered advantageous to have a maximum number of multiple bonds, which can be accomplished in linear molecules and organic rings by alternating the single and double bonds (polyconjugation). The presence of a maximum number of multiple conjugated bonds in the macromolecule with a comparatively weak bond of the electrons to the atoms would facilitate the increase in electroconductivity. It is considered expedient to introduce atoms with a relatively weak bond of the electrons on the outer orbits, in order to decrease the width of the forbidden zone. The conductivity is further dependent on the migration of the double bonds and thus it is also expedient to increase the number of possible migrations of this kind, forming comple cyclic structures of conjugated bonds, (e.g., phthalocyanine and the metal compound type). In a molecule having quasi-free electrons the possibility of electronic and hole-type conductivity is present. The authors attempt to give a rough evaluation of the cases: Thus in the case of a double bond the π-electrons are less firmly attached to the corresponding atoms or group of atoms than

the σ-electrons and more mobile, and thanks to the quantum tunnel effect can overcome the barrier U(r) and move to a neighboring bond with a probability p (relative to a unit of time)

$$\frac{1}{\tau} \sim p \approx \frac{V}{L} \exp\left\{-\frac{2}{-h-}\int_{r_1}^{r_2}\sqrt{2m[U(r)-\varepsilon]}\,dr\right\} \quad (A),$$

where τ is the life-span of the electron on a separate bond, $-h- = \frac{h}{2\pi}$, L is the width of the potential depression, where the electrons are located, m is the electron mass, V is its velocity, ε is the kinetic energy. The complex function U(r) is replaced for simplicity by a rectangular potential barrier (Fig. 1), then L is determined by the length of the double bond C=C, U_o is determined by the dimensions of the atom C, $U_o - \varepsilon$ by the potential energy of the most weakly bonded electron. Then equation (A) becomes:

$$\tau \approx \frac{1}{V} \exp\left\{-\frac{2}{-h-} L_o \sqrt{2m(U_o - \varepsilon)}\right\}.$$

At $L = T \cdot 10^{-8}$, $U_o - \varepsilon = 10$ ev $= 10^{-8}$ cm/sec, we obtain $\tau = 10^{-15}$ sec. Thus during the time of the electron being locat-

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ed on one bond about 10^{-15} it shifts over at a rate of $V_{shift} = \frac{10^{-8}}{10^{-15}} = 10^{7}$ cm/ sec. The given formulas show that due to the strong dependence of τ on U_0 and $U_{max.} - \mathcal{E}$, the electrons of the internal orbits forming the polymer molecule, which have a greater bond energy, will be almost completely localized and will not be able to participate in the electroconductivity of the macromolecule. It is stressed that the problem of the transfer of the charge carriers (electrons and holes) from molecule to molecule is a difficult one. It is assumed that the mobility of the charge carriers can be mainly determined by the probability of the tunnel gap through the intramolecular barrier and that high temperatures are necessary so that the electrons can overcome these gaps between the macromolecules. The electroconductivity of the polymer semiconductor will depend only on the concentration of the charge carriers in the first approximation (at a given structure of the polymer). The importance of the intramolecular transfers is stressed on the example of the benzene molecule, which is an excellent conductor, but liquid benzene (a group of these molecules) is an excellent insulator. The actual potential barrier between the macromolecules depends on these conditions, i.e., on the distance between the macromolecules and their number in a unit volume. The

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chemical bonds between the molecules and their space orientation will also become relevant factors in future. The optimum conditions for the formation and movement of charge carriers in the macromolecule is partly determined by the formation of the polymer molecule with polyconjugated and aromatic rings in the chain, but the latter do not solve completely the problems of easing the intramolecular barrier for them. Further mention is made of the significant effect of orientation on the electroconductivity of the polymer. The orientation of the polymer molecule also causes severe anisotropy of its properties along and across the axis of orientation. As regards the electroconductivity, it is assumed that the orientation can lead to two results: an increase in the number of charge carriers passing in a unit of time through a certain transverse cross-section of the polymer semiconductor, and the occurrence of severe anisotropy of the conductivity. In a polymer with regularly-built chains the conductivity is present only in the chain molecules. It is suggested that the conducting elements can be simply arranged parallel to each other, and thus create a system with good conductivity along the orientation axis and a slight conductivity in the perpendicular direction. The most expedient conditions are a high degree of regularity and few transverse bonds, since the latter would form the most perfected orientation of the polymer thread. This type of polymer system should have the best conductivity along

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the orientation axis and the highest anisotropy of the conductivity. The authors discuss the paramagnetic properties of semiconductors, particularly occurring in their spectra of electronic paramagnetic resonance (EPR). Since the integral EPR spectrum is connected with the number of electrons present having non-paired spins in the investigated system, it is assumed that the π-cloud is characterized by a certain non-pairing. The number of particles with non-paired spins corresponding to the narrow signal in the EPR spectrum of the polymer is about 10^{18}-10^{19} in one cm^3. But these cannot be considered charge carriers in polymers with semiconductor properties for the following reason: the electroconductivity increases with the temperature and the concentration of these particles determined by the area of the narrow line mentioned in the EPR spectrum drops. It is assumed that the second wide signal might be connected with the electroconductivity. The EPR spectrum is considered a property of the modecule and not of the polymer on the whole. The signal in the EPR spectrum indicates the fulfillment of an important, although not the only, condition for the polymer (especially synthesized or processed), to possess semiconductor properties. The presence of a system of conjugated double bonds is considered important but not adequate for the formation of a polymer material, which would completely be conducting, particu-

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larly semiconducting. The authors claim that it is possible to produce polymers with a system of conjugated bonds in the main chain in two ways: 1) by transformation of the macromolecules in the chain of already known polymers, 2) by special construction (synthesis) of the macromolecules with a system of conjugated bonds. Some of the specific work done on the synthesizing of polymer molecules with a system of conjugated bonds is gone into, particularly that of the products of thermal transformation of polyacrylonitrile. It is thought that interesting prospects lie in the production of this polymer substance characterized by a complex of electrophysical properties, viz., semiconductivity. It is assumed that in the thermal transformation the polyacrylonitrile undergoes chemical changes leading to the formation of a polymer, the macromolecules of which consist of cyclic chains. The given reaction schemes show that in this type of polymer semiconductivity properties can be expected. This corresponds to the theory developed by Semenov (Ref. 7) in analyzing the EPR spectra of certain polymer molecules, especially that of polyaminoquinone. When elevating the temperature of processing the polyacrylonitrile, the narrow signal of the EPR mentioned above increases (Fig. 3) almostly linearly in the temperature range of 325-600°C. Similar data were previously obtained in the thermal processing of polyvinylchloride (Ref. 10). The authors feel partially justified in assuming that in order to produce

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satisfactory semiconductor properties, a strict regularity of the structure of the polymer chains is needed. It is also assumed that polyacrylonitrile forms such regular chains. Special interest is felt in orientation as a means for increasing the regularity of the structure of polymers amongst other possibilities. The authors specify that at the present time several new polymer materials, the macromolecules of which have a system of conjugated double bonds, have been produced both in the USSR and abroad. These polymers have interesting magnetic properties. In this connection the work of Berlin (Ref. 15) is noted in the synthesis of polyaminoquinones. In the interaction of chloranil with benzidine polymers were obtained of the given structure. The authors of this synthesis assume that in this case there are not only intermolecular hydrogen bonds, but also bonds of the intrachain type, which can lead to spatial structuralizing and impairment of the solubility. Reference is also made to polymer-chelate complexes of percyanoethylene with metals (Ref. 21) stating that these compounds have a high thermal stability, a high magnetic susceptibility, a low activation energy, (0.26) and σ about 10^{-2} $ohm^{-1} \cdot cm^{-1}$ at 20°C. Special attention is further paid to the products synthesized by the authors (Ref. 16) of semi-condensation of phthalic anhydride with n-phenylenediamine and hydroquinone. The latter are

Semiconductor Properties of Polymer Materials

characterized by an electroconductivity of $7 \cdot 10^{-7}$ ohm^{-1}.cm^{-1} with an activation energy of about 0.6 ev. Roginskiy (Ref. 18) mentioned the interesting possibilities of using the semiconducting properties of certain organic polymers as heterogenic catalysts. Semenev (Ref. 20) studied this matter further. In conclusion the authors point out that the future profound investigation of the properties of polymer materials with a system of conjugated bonds, especially those with obvious semiconducting properties, will lead to new possibilities of creating heterogeneous catalysts with a high selectivity. There are 2 figures, 1 table, 5 structural formulae, 1 diagram, 3 equations and 21 references: 14 are Soviet, 6 English, 1 Belgian.

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B162/B101

5,1190
15,8063

AUTHORS: Pokatilo, N. A., Yerasova, Ya. L., Unmut, A. M., Krentsel', B. A., Topchiyev, A. V.

TITLE: Production of isotactic polybutylene

PERIODICAL: Referativnyy zhurnal. Khimiya, no. 6, 1962, 615, abstract 6P43 (Tr. In-ta nefti. AN SSSR, v. 14, 1960, 58-64)

TEXT: An investigation is made of the polymerization reaction of α-butylene using two systems of complex organo-metallic catalysts: $Al(C_2H_5)_3 + TiCl_4$ and $Al(iso\text{-}C_4H_9)_3 + TiCl_4$. The polymerization reaction of α-butylene was carried out in a medium of n-heptane, cleansed of moisture and unsaturated compounds. It is established that the best conditions for the production of isotactic α-polybutylene with the catalyst $Al(C_2H_5)_3 + TiCl_4$ are: molar ratio $(C_2H_5)_3Al:TiCl_4 = 8:1$, reaction temperature 20-30°C, reaction time 3 hrs; with the catalyst $Al(iso\text{-}C_4H_9)_3 + TiCl_4$ they are: molar ratio $(iso\text{-}C_4H_9)_3Al:TiCl_4 = 1:1$, reaction temperature 20-30°C, reaction time 5 hrs. An attempt is made to

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Production of isotactic ...

carry out polymerization of α-butylene in the liquid phase at temperatures and pressures close to the critical ones, in a β-butylene medium and also in a part of the α-butylene not involved in the reaction, using the catalytic system $Al(C_2H_5)_3 + TiCl_4$. [Abstracter's note: Complete translation.]

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S/081/62/000/003/078/090
B160/B101

AUTHORS: Topchiyev, A. V., Krentsel', B. A.

TITLE: Modern methods of using petroleum and gas to produce high-polymer products

PERIODICAL: Referativnyy zhurnal. Khimiya, no. 3, 1962, 560 - 561, abstract 3P18 (Tr. Groznensk. neft. in-t, sb. 23, 1960, 5 - 20)

TEXT: The future possibilities of producing polymers based on petroleum and gas and the most important trends in petrochemical synthesis in the coming years are discussed. The results are given of the authors' work on producing polypropylene and polyethylene and their study of the nature of the catalytic activity of chromium oxide and molybdenum oxide catalysts. The possibility of extensive use of nuclear irradiation in polymerization and other petrochemical synthesis processes is mentioned. [Abstracter's note: Complete translation.]

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S/030/60/000/05/15/056
B015/B008

AUTHORS: Kargin, V. A., Krentsel', B. A., Rokhlin, M. I., Smirnov, V. S.

TITLE: International Symposium on Macromolecular Chemistry and the Exposition of Synthetic Materials in the German Federal Republic

PERIODICAL: Vestnik Akademii nauk SSSR, 1960, No. 5, pp. 68-74

TEXT: The Symposium was convened by the Commission of High-molecular Compounds of the International Association for Pure and Applied Chemistry and was held at Wiesbaden (German Federal Republic) from October 12 to 17, 1959. It was attended by some 1200 scientists from 22 countries. The Soviet delegation consisted of 29 representatives of the main branches of the chemistry and physics of polymers of the USSR. Problems of the physics of the polymers, high-molecular compounds in solutions, the elementary acts as well as the kinetics of polyreactions, the chemistry of organic and inorganic high-molecular compounds, the natural high-molecular compounds and models were discussed. G. P. Mikhaylov

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International Symposium on Macromolecular Chemistry and the Exposition of Synthetic Materials in the German Federal Republic

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reported on the investigation results of the molecular relaxation in polymers by means of the dielectric method. V. A. Kargin stated that the globules are to be considered as primary elementary structures in the orientation and crystallization of polymers. S. S. Medvedev showed that the development of cationic chains is directly linked with the formation of complexes between the catalyst and monomer. G. Mark (USA) mentioned in his report papers by Soviet scientists, especially the investigations by K. A. Andrianov in the field of the synthesis of organosilicon polymers. The authors describe next the International Exposition of Synthetic Materials which was held at Duesseldorf from October 17 to 25, 1959, and at which 21 countries (over 670 firms) were represented. The authors state that about one half of the exhibits consisted of machines and the other half of finished products. Among synthetic materials, polyvinyl chloride, polyethylene and reinforced plastics are especially mentioned, the authors referring to the papers by V. A. Kargin and N. A. Plate. It is underlined finally that the work of the experts in the field of new processing methods is to be regarded as being as important as the creation of new polymers. There is 1 Soviet reference.

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B010/B015

AUTHORS: Frenkel', S. Ya., Topchiyev, A. V., Krentsel', B. A., Gol'dfarb, Yu. Ya.

TITLE: Investigation of the Polydispersity of Polymers by the Method of the Unestablished Sedimentation Equilibrium. II. Investigation of Polyisobutylene Obtained With a Complex Organometallic Catalyst

PERIODICAL: Zhurnal fizicheskoy khimii, 1960, Vol 34, Nr 2, pp 327-334 (USSR)

ABSTRACT: The investigation results of the previous paper (Ref 1) were completed by determining the sedimentation coefficients S, diffusion coefficients D, and characteristic viscosities $[\eta]$ on 5 polyisobutylene samples in n-heptane at 20° and at 1 atm. The values of measurement obtained for these hydrodynamic characteristics are given (Table 1). Three of the samples showed a noticeable polydispersity. The molecular weights were calculated according to the formulas:

$D([\eta]M)^{1/3} = 2{,}56\cdot10^{-5}$ $S([\eta]M^2)^{1/3} = 2{,}47\cdot10^{-16}$ Svedberg (Table 2), and it was found that $S = 2.57\cdot10^{-2} M_{SD_{2m}}^{1/2}$ units; $D = 2.63\cdot10^{-4} M_{SD_{2m}}^{1/2}$ cm^2/sec, and $[\eta] = 7\cdot10^{-6} M_{S[\eta]}$ hold for the unfractionated samples, i.e. for the dependence of the

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S/076/60/034/02/010/044
B010/B015

Investigation of the Polydispersity of Polymers by the Method of the Unestablished Sedimentation Equilibrium. II. Investigation of Polyisobutylene Obtained With a Complex Organometallic Catalyst

characteristic viscosity $[\eta]$ on the mean molecular weight $M_{S[\eta]}$ the simple Staudinger equation is obtained. The values for M_w and M_z were taken from reference 1, and indicated together with those for M_{SD} and $M_{S[\eta]}$, as well as M_o (Table 3). A simple method is suggested for the correlation of the hydrodynamic values of measurement with the direct values of measurement for M_z and M_w, and it is pointed out that a similarity to the distribution function, given by Wesslau (Ref 7) for some of the low-pressure polyethylenes, may be observed. If all conditions remain the same, the molecular weight of polyisobutylene increases with the duration of the polymerization reaction. This fact indicates a successive prolongation of the linear chains. The growing of molecules on catalysts of the Ziegler-Natta type is assumed to be comparable with the "growing of a tree". The degree of polymerization depends on the duration γ of the growing process and the rate of growth v. The values γ and v are determined by the properties of the ternary system monomer - catalyst - solvent. Studies in connection with the Krämer-Lansing distribution function lead to the con-

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68848

Investigation of the Polydispersity of Polymers by the Method of the Unestablished Sedimentation Equilibrium. II. Investigation of Polyisobutylene Obtained With a Complex Organometallic Catalyst

S/076/60/034/02/010/044
B010/B015

clusion that the samples investigated exhibit rather a high dispersity. It is doubted that the free radicals play an essential part in the process investigated. There are 5 figures, 3 tables, and 12 references, 6 of which are Soviet.

ASSOCIATION: Akademiya nauk SSSR Institut vysokomolekulyarnykh soyedineniy (Academy of Sciences of the USSR, Institute of High-molecular Compounds). Institut neftekhimicheskogo sinteza (Institute of Petroleum-chemical Synthesis)

SUBMITTED: April 21, 1958

Card 3/3

5.3831

5(3)

SOV/20-130-2-28/69

AUTHORS: Topchiyev, A. V., Academician, Mushina, Ye. A., Perel'man, A. I., Krentsel', B. A.

TITLE: Synthesis of Polyvinylcyclohexane

PERIODICAL: Doklady Akademii nauk SSSR, 1960, Vol 130, Nr 2, pp 344 - 345 (USSR)

ABSTRACT: There are no publication data on the polymerization of the vinyl derivatives of cyclohexane. Therefore, the authors wanted to investigate the possibility of producing polyvinylcyclohexane, and the influence of the nature of the catalyst on the properties of the polymer. Vinylcyclohexane was obtained from the cyclohexylethyl alcohol (Ref 1, see Scheme). This alcohol was synthesized in 2 ways: I) by the action of an absolutely dry gaseous ethylene oxide on magnesium chlorocyclohexane (produced by the Grignard reaction) in ethereal solution (Refs 2,3); II) by hydrogenation of phenylethyl alcohol on Raney's nickel catalyst at 160° and a pressure of 100 atm. The yield was ~ 50%. Vinylcyclohexane was obtained by acetylation of the cyclohexyl alcohol and by pyrolysis of the acetate (Ref 1). 2 catalysts

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Synthesis of Polyvinylcyclohexane

SOV/20-130-2-28/69

were used for the polymerization of the vinylcyclohexane: a) a chromic-oxide-, and b) an organo-metallic catalyst. Carefully dehydrated heptane or benzene was used with a) as a solvent for the monomer. The authors' experiments showed that an addition of triisobutyl aluminum (50% solution in heptane) doubles the polymer yield. The properties (crystallinity, viscosity, etc) remain unchanged (Fig 1 a, b, p 318). The polymerization b) was carried out in a current of purified nitrogen at 80°. Triisobutyl aluminum with titanium tetrachloride was used as a catalyst. According to preliminary data, the polymer yield was ~ 30%. No ash content was found in the product polymerized on the chromic-oxide catalyst. The product polymerized on $(iso\text{-}C_4H_9)_3$ + $TiCl_4$ contains 1% of ashes. Polyvinylcyclohexane is a white, finely-disperse powder melting at 325°, and soluble in organic solvents. The characteristic viscosity was different depending on the nature of the catalyst used: it was 0.5 for a), and 1 - 1.5 for b). The elementary analysis in % yielded: C 87.22 (computed 87.27); H 12.80 (computed 12.72). The roentgenograms showed a high crystallinity of

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Synthesis of Polyvinylcyclohexane 30V/20-130-2-28/69

the polymer (Fig 1). Finally, the authors give a scheme for the presumable structure of the polymer. No by-products of the reaction were ascertained in the polymerization mentioned. There are 1 figure, 1 table, and 7 references, 6 of which are Soviet.

SUBMITTED: September 3, 1959

Card 3/3

To be submitted for the International Symposium on Macromolecular Chemistry, Montreal, Canada, 27 Jul -1 Aug 1961.

USSR

BIRSHTEYN, T. M., Institute of High Molecular Chemistry, Academy of Sciences USSR, Leningrad, jointly with KRIGBAUM, W. R., and KANEKO, M., Duke University, Durham, N.C. - "Elasticity of cube lattice chain networks" (Group 2)

DOGADKIN, Boris A., and DONTSOV, A. A., Moscow Institute of Fine Chemical Technology imeni M. V. Lomonosov - "Interaction of polyethylene with sulphur" (Groups 4-5)

KARGIN, Valentin A., Head, Laboratory of Colloidal Chemistry, Scientific Research Physico-Chemical Institute imeni L. Ya. Karpov, Moscow - "The formation of big crystal structures in polymers and their properties" (Group 2. Invited lecture)

KREYTSEL', B. A., TOPCHIYEV, A. V., and RAKALO, L. I., Institute of Petroleum, Academy of Sciences USSR, Moscow - "Polymerization of some epoxy compounds" (Group 3-B)

MEDVEDEV, Sergey S., SPIRIN, Yu. A., AREST-YAKUBOVICH, A. A., POLYAKOV, D. K., and GANTMAKHER, A. R., Scientific Research Physico-Chemical Institute imeni L. Ya. Karpov, Moscow - "Polymerization catalyzed by lithium and lithium alkyl" (In German) (Group 3-B)

NAMETKIN, N. S., TOPCHIYEV, A. V., and POLAK, L. S., Institute of Petrochemical Synthesis, Academy of Sciences USSR, Moscow - "On the catalytic polymerization and radiochemistry of allylsilans" (Group 3-A)

PIOTROVSKIY, K. B., All-Union Scientific Research Institute of Synthetic Rubber imeni S. V. Lebedev, Leningrad - "Temperature effect on polymer structure in diene polymerization by alkali metals" (Group 3-B)

PODDUBNYY, I. Ya., and YERENBURG, Ye. G., All-Union Scientific Research Institute of Synthetic Rubber, Leningrad - "Study of branching in regular isoprene polymers" (Group 1)

PODDUBNYY, I. Ya. MOKEYEVSKIY, M. F., RABINERZON, M. A., and PROKOF'YEV, A. [illegible] All-Union Scientific Research Institute of Synthetic Rubber imeni S. V. Lebedev, Leningrad - "Nature of molecular-weight distribution and properties of styrene-butadiene rubbers depending on polymerization conditions" (Group 3-A)

PRAVEDNIKOV, A. N., TELESHOV, Ye. N., YING, Shu-k'ang, and MEDVEDEV, S. S., Scientific Research Physico-Chemical Institute imeni L. Ya. Karpov, Moscow - "Investigation of the mechanism of radiolysis of polymers containing quaternary atoms of carbon" (Group 4-5)

TSVETKOV, Viktor N., Institute of High Molecular Compounds of the Academy of Sciences USSR, Leningrad - "Stereo-regularity and optical anisotropy of macromolecules" (Group not specified)

USMANOV, Khamdam U., and SHUMKEVICH, [illegible], Academy of Sciences UzSSR, Tashkent, Uzbekistan - "The investigation of the cotton cellulose polydispersity according to the molecular weight" (Group not specified)

YENIKOLOPYAN, N. S., Institute of Chemical Physics of the Academy of Sciences USSR, Moscow - "On the kinetics of formaldehyde polymerization and polyformaldehyde degradation" (Group 3-B)

15.8610

31668
S/607/61/003/000/001/002
E075/E185

AUTHORS: Topchiyev, A.V., and Krentsel', B.A.

TITLE: Some rules concerning the polymerization of α-olefines on metallo-organic and metal oxide catalysts

SOURCE: International Petroleum Congress. 5th, New York, 1959 (Doklady) t. 3: Pererabotka nefti i gaza. Neftekhimiya. Moscow, Gostoptekhizdat, 1961. 323-333

TEXT: In order to discover the mechanism of stereo-specific polymerization and the role of different catalysts therein, investigation was carried out of the mechanism of the polymerization of propylene, α-butene and ethylene with the use of metallo-organic and metal oxides as catalysts. In the polymerization of propylene an important characteristic of the catalysts used, i.e. AlR_3 + $TiCl_4$, is the rapid fall in its activity. This distinguishes it from another system of catalysts, AlR_3 + $TiCl_3$, which does not change its activity with time. It was confirmed that the polymerization of propylene is more effective if the alkyl aluminium is added gradually to the reaction mixture already containing $TiCl_4$. The application of this method gives 40-fold

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Some rules concerning the ....

increase in yield of polypropylene. Oxygen dissolved in propylene strongly affects yields of polypropylene. It was found that when the concentration of oxygen reaches 0.05 mole %, the yield of polypropylene grows markedly. Further increase in the concentration of oxygen leads to a lowering in yields of the polymer. It was concluded that free radical mechanism holds for the reaction and that small amounts of oxygen facilitate the formation of free radicals in the reaction mixture which gave the increased yields. The reaction was represented schematically as follows:

$$TiCl_4 + AlR_3 \rightarrow RTiCl_3 + R_2AlCl; \quad RTiCl_3 \rightarrow R^{\circ} + TiCl_3$$

It is not thought that this mechanism may necessarily apply to the reaction if it proceeds under different conditions. Another reaction studied was the polymerization of α-butene, with triethylaluminium plus titanium tetrachloride as catalyst. It was found that the ratio of AlR_3 to $TiCl_4$ influences radically the molecular weight and crystallinity of the polymer. The highest molecular weight is obtained for the ratio of

$$Al(C_2H_5)_3 : TiCl_4 \approx 8 : 1$$

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31668
S/607/61/003/000/001/002
E075/E185

Some rules concerning the ....

The polymerization of ethylene was studied with the simultaneous formation of triethylaluminium, lithiumhydride and aluminium chloride. The reaction proceeded well providing the solvent and the temperature of the reaction were chosen so as to avoid the deposition of polyethylene on the unreacted lithium hydride. The formation of crystalline polyethylene and polypropylene using chromium oxide and molybdenum oxide catalysts was investigated, paying special attention to the effect of activation temperature on the activity of the catalysts. It was found that with the increasing temperature of activation, from 300 to 650 °C, the quantity of hexavalent chromium decreases. An active form of the oxide was obtained by heating between 500 and 600 °C which gave a mixture of CrO_3 and Cr_2O_3, the latter oxide being associated with the active oxygen. The active and inactive forms of the catalysts could be readily recognized by the application of thermal analysis, the active form giving a number of endothermic and exothermic effects on heating, whilst the inactive form did not give any heat effects. The most active catalyst consists of chromium oxide having the empirical formula of $CrO_{2.4}$.

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Some rules concerning the ...

As previously, it was found that an excess of solvent (20:1 - 30:1) facilitates the polymerization process by dissolving the polymer from the surfaces of the catalysts. The polymerization of ethylene with molybdenum oxide as catalyst was carried out at 220 to 240 °C and 50 to 75 atm pressure. The catalyst contained 10% MoO_3 and was prepared by heating γ aluminium oxide with ammonium molybdate solution. The experiments were conducted with the addition of LiH (3% of the weight of the catalyst); CaH_2, metallic Na tributylaluminium were also added in some experiments. It was found that by changing the temperature and pressure of the reaction it was possible to control the properties of the resulting polymers. Under suitable conditions polymers with molecular weight of 10 000 to 500 000 and softening temperature 125 to 215 °C could be obtained.
There are 7 figures, 2 tables and 13 references: 4 Soviet-bloc and 9 non-Soviet-bloc. The four most recent English language references read as follows:

Card 4/5

Some rules concerning the S/607/61/003/000/001/002
E075/E185

Ref.3: I.R. Stille. Polymerization of olefines by complex metal catalysts. Chem. Reviews, 58, 541, 1958.

Ref.5: G. Natta. Kinetic studies on alpha-olefine polymerization. Report to the International High-Polymer Conference, Nottingham, July 21-24, 1958.

Ref.7: A. Orzeschowski. A study of the formation and performance of triisobutyl aluminium - $TiCl_4$. Ziegler catalyst in ethylene polymerization. Report to the International High Polymer Conference, Nottingham, July 21-24, 1958.

Ref.9: J.C. McGowan, B.N. Ford. Polymerization of ethylene in the presence of titanium tetrachloride and certain metal alkyls. J. Chem. Soc., no.3, 1949, 1958.

Card 5/5

89689

S/026/61/000/001/004/007
A166/A027

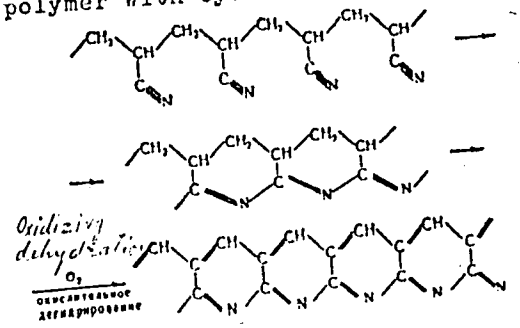
15.8105
9,4300 (1164, 1143 only)

AUTHOR: Krentsel, B.A., Doctor of Chemical Sciences

TITLE: Organic Semiconductors

PERIODICAL: Priroda, 1961, No. 1, pp. 51-55

TEXT: The author explains the theory and properties of organic semiconductors and describes some new types developed by Soviet scientists. Academician A.V. Topchiyev and V.A. Kargin, in their studies of the electrophysical properties of polyacrilonitrile, have found that heat treatment leads to the formation of a new polymer with cyclic structure and system of conjugate bonds as follows



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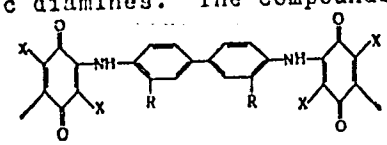
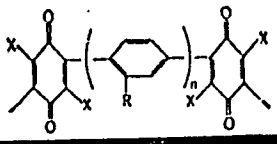
89689

S/026/61/000/001/004/007
A166/A027

Organic Semiconductors

This gives material with semiconductor properties and electrical conductivity at room temperature ranging from 10^{-10} - 10^{-3} ohms^{-1} cm^{-1}. All these polymers have the characteristic semiconductor relation of temperature to electrical conductivity and a characteristic spectrum of electron paramagnetic resonance. Topchiyev and Kargin have shown that heat treatment of polyacrilonile in an ammonium atmosphere leads to a considerable increase in electrical conductivity. The introduction of metallic salts into the macromolecule (before conversion) also enhances conductivity, with a simultaneous increase in activation energy. A.A. Berlin has obtained polymers with conjugate bond systems and interesting electrophysical properties in reactions of aromatic compounds, e.g., chloranil with diaminodiphenyl or benzoquinone with aromatic diamines. The compounds had the following structure:





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Organic Semiconductors

S/026/61/000/001/004/007
A166/A027

where X is the haloid and R the hydrogen, alkyl group, COOH, etc. These polymers have comparatively high magnetic susceptibility, varying with the intensity of the magnetic field. Berlin has also synthesized complex polymer compounds of a structure similar to that of phthalocyanin, consisting of carbon, nitrogen and metals and characterized by high dielectric constant and magnetic susceptibility. Their conductivity range is $\sigma_0 = 10^{-2}$ ohms^{-1} cm^{-1}. An interesting aspect is that the polymer may be synthesized directly on the surface of the metal forming a continuous, firmly bonded film. The increase in conductivity noted in the heat treatment of polymers with conjugate double bonds may be due to the formation of peculiar bridges between the individual macromolecules, thus improving macromolecular contact. Topchiyev and Kargin have proved that orientation (chain distribution) of the macromolecules in the polymer has a definite effect on electrical conductivity.

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S/191/61/000/002/001/012
B118/B203

AUTHORS: Topchiyev, A. V., Krentsel', B. A., Sidorova, L. G.

TITLE: Polymerization of propylene with the catalytic system $Al(iso\text{-}C_4H_9)_3 + TiCl_4$

PERIODICAL: Plasticheskiye massy, no. 2, 1961, 3 - 8

TEXT: For some modes of application of polypropylene (films, tubes) a high content of isotactic structure (produced by the catalytic complex containing $TiCl_3$) is not required; the quality of the stereoblock polymer obtained with the catalytic system $AlR_3 + TiCl_4$ is sufficient. This circumstance induced the authors to study the polymerization of propylene with the system $Al(iso\text{-}C_4H_9)_3 + TiCl_4$. They proceeded from the industrial propylene-propane fraction of the gas formed in petroleum pyrolysis which contained practically no oxygen after thorough purification (Ref.1). Triisobutyl aluminum was distilled in vacuo, and used as a 20-30 % solu-

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Polymerization of propylene ...

tion in purified benzine fraction boiling between 90 and 110°C. Commercial titanium tetrachloride was "chemically pure". The components were stored in a vessel filled with pure nitrogen. The propylene polymerization was performed in inert, carefully purified, anhydrous n-heptane as solvent. It proceeded successfully with the complex catalyst $Al(iso\text{-}C_4H_9)_3 + TiCl_4$ which is less inflammable and better accessible than the hitherto used $Al(C_2H_5)_3 + TiCl_4$. The molar ratio K between the components of the catalyst affects the yield and the molecular weight of polypropylene. The maximum yield of polymer was obtained at K = 1.5 : 2 moles of triisobutyl aluminum/$TiCl_4$. The highest-molecular polypropylene was formed at K = 3. The catalytic activity of the complex catalyst decreases with time due to a change in its composition, irrespective of whether it is in operation or stored in an inert medium. If, however, the propylene polymerization is performed by bringing about a gradual formation of the catalyst complex with a steady addition of small doses of $Al(i\text{-}C_4H_9)_3$, then the high activity of the catalyst is preserved lon-

ger, and yields are much higher without any change in the mean molecular weight. Yield and molecular weight of polypropylene decrease in the range of 20-90°C with increasing test temperature. The ratio between the atactic and isotactic fractions does not change during the reaction. The oxygen existing in the initial propylene affects the polypropylene yield; maximum yield is attained at a content of 0.05 mole% of oxygen. The higher activity of the catalyst in the presence of oxygen may be explained by the circumstance that oxygen converts the catalytic system to a redox system. N. A. Nechitaylo assisted in the experiments. There are 9 figures, 1 table, and 20 references: 6 Soviet-bloc and 12 non-Soviet-bloc.

Card 3/3

23768

S/190/61/003/006/011/019
B110/B208

15.8111 2209

AUTHORS: Topchiyev, A.V., Col'dfarb, Yu. Ya., Krentsel', B. A.

TITLE: Polymerization of some heterocyclic compounds in the presence of a complex organometallic catalyst

PERIODICAL: Vysokomolekulyarnyye soyedineniya, v. 3, no. 6, 1961, 870 - 876

TEXT: Three-membered rings were opened in the heterocyclic compounds polymerized by the authors (Ref. 1: Izv. AN SSSR, Otd. khim. n., 1959, 369) by means of a complex organometallic catalyst (ethylene oxide, ethylene imine etc.). By substitution of other heteroatoms for the heteroatom (e. g. of sulfur for the furan oxygen) the aromatic character is changed and the ring opening in the polymerization of thiophene should not take place. The purpose of the present paper was therefore the investigation of furan, α-methyl furan and thiophene polymerizations and that of their homologs by the new metalalkyl titanium tetrachloride catalysts. Their copolymerization with olefins should also be studied later on. The authors also investigated the polymerization of dihydropyran which like furan was obtained in a high yield. The polymerization of furan took

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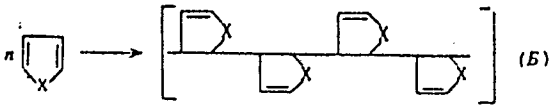
B110/B208

Polymerization of some heterocyclic ...

place between 0 and 25°C with the $Al(C_2H_5)_3$+$TiCl_4$ catalyst whose ratios fluctuated between 3:1 and 1:5 and whose concentration (referred to the solvent) between 1 and 12%. The yield increased with the $TiCl_4$ content in the catalyst, partial resinification occurred with a ratio of 1:5. Temperature changes between 10 and 25°C did not affect the yield which, however, drops at $\geq$ 0°C. An optimum yield of the polymer of the accessible α-methyl furan (silvan) was obtained at 10°C (Fig. 1 a), at a molar ratio $Al(C_2H_5)_3$:$TiCl_4$=1:5 (Fig. 1б), and at a catalyst concentration of 12%. The optimum ratio for furan was 1:3. Under similar conditions (temperature =75°C) thiophene gave lower optimum yields. The best yields were obtained for dihydropyran at a ratio 1:1$_2$ and 20°C. Samples of polyfuran and polysilvan were pressed at 20 kg/cm^2 at 100°C, and their thermomechanical curves were recorded by means of the dynamometric weights of Kargin. At ~90°C, cross linking, decrease of deformation and hardening took place. This is indicative of double bonds in the chain and sufficient mobility in the links which also becomes manifest at the vitrification temperature. A viscous state is prevented by the network. At a softening point of the polymers between 220 and 230°C deformation increases, then becomes constant

Polymerization of some heterocyclic ...

up to decomposition at 350°C. The high-elastic state lies between 90 and 230°C. X-ray examination disclosed an amorphous structure. Absorption spectra were taken by M. V. Shishkina on the ИКС-14 (IKS-14) spectrograph in the laboratory of M. M. Kusakov of the authors' institute. The presence of double bonds and the absence of the diene system were confirmed. The authors assume the following structure for the polymers of thiophene, furan and silvan:



(5)

As no ring opening occurs in reactions of thiophene, furan and their homologs with Friedel-Crafts catalysts, it is not assumed in this case either. This is also supported by the high decomposition temperature and the results of spectrum analysis. 60 ml of n-hexane, purified by sulfuric acid and distilled over metallic sodium were mixed with 3.98 $TiCl_4$ and 0.82g $Al(C_2H_5)_3$ under stirring at a temperature kept constant at 10°C

by means of a Höppler thermostat. After 3 min the catalyst was added, and within 10 min 8.2g furan. After 6 hours the catalyst is destroyed by CH_3OH, and the polymer is dried at 160°C and 4 mm Hg up to weight constancy. 1.62 g of a yellow solid and 0.76 g of a liquid product were obtained. 4-methyl furan (boiling point 63.5°C, n_D^{20}=1.4310) was polymerized in an analogous way. 2.64 g of a light brown polymer were separated by n-hexane from the ether extract of the polymer dried by $CaCl_2$. After evaporation of the ether 3.4 g low-molecular polysilvan with an intrinsic viscosity of 0.15 (in dioxane at 30°C) with 72.62%C; 7,64% H was left. 1.7 g $TiCl_4$ and 0.13g $Al(C_2H_5)_3$ were added to 15 ml n-hexane. 2.1 g thiophene were added 3 min after addition of the catalyst. The resultant powdery yellow polythiophene decomposed at ~180°C and had a viscosity of 0.11: 58.6%C; 4.74%H. 0.75 g $TiCl_4$, 0.45 g $Al(C_2H_5)_3$ and 2.1 g dihydropyran were added to 15 ml n-hexane. The white, powdery polyhydropyran formed in a 0.46 g yield decomposed at 110°C and had the composition: 68.82%C; 9.67%H.

There are 4 figures, 5 references: 3 Soviet-bloc and 2 non-Soviet-bloc. The references to English-language publications read as follows: Ref. 2: J. Bruce, F. Challenger, H. B. Gibson, W. E. Allenby, J. Inst. Pet. Techn., 34, 226, 1948. Ref. 3: S. L. Meisel, G. C. Jonson, H. D. Hartough, J. Amer. Chem. Soc., 72, 1910, 1950.

ASSOCIATION: Institut neftekhimicheskogo sinteza AN SSSR (Institute of Petrochemical Synthesis AS USSR)

SUBMITTED: July 28, 1960

158061

25261

S/190/61/003/007/005/021
B101/E208

AUTHORS: Il'ina, D. Ye., Krentsel', B. A., Topchiyev, A. V.

TITLE: Sulfochlorination of polypropylene

PERIODICAL: Vysokomolekulyarnyye soyedineniya, v. 3, no. 7, 1961, 995-999

TEXT: The purpose of the present study was the modification of polypropylene (PP) by photochemical sulfochlorination. PP was synthesized as stereoblock polymer by $Al(C_2H_5)_3 + TiCl_4$ catalyst. Its softening temperature was 168-172°C, its intrinsic viscosity (determined in decaline at 120°C) 1.55, it contained 2% amorphous fractions soluble in boiling ether. PP was thoroughly mixed with CCl_4 at 60-65°C, the amorphous part dissolved after 1-1.5 hr, the high-molecular part formed a stable suspension. It was then exposed (in all experiments) to a 200 w lamp, and $Cl_2 + SO_2$ was bubbled through the suspension in different ratios. The finished product was a fine-dispersed white powder. The

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Sulfochlorination of polypropylene 25261

S/190/61/003/007/005/021
B101/B208

following was studied: 1) temperature influence. By bubbling with $Cl_2 + SO_2$ in a ratio of 3 : 1 (3 l/hr Cl_2, 1 l/hr SO_2) and variation of the temperature between 0-70°C, the following was found: a) When temperature is raised from 35 to 70°C, the Cl_2 content in the end product remains constant (47.92%), and the sulfur content decreases (from 2.7 to 1.42%). b) If the temperature is reduced from 35 to 0°C, the Cl_2 content decreases to 19.29%. and the S content increases to 6.61%. 2) Effect of the ratio of the reagents on the Cl_2 and S quantities absorbed by PP at 25°C. Experimental series A: Constant Cl_2 supply (3 l/hr) and variation of the Cl_2/SO_2 ratio between 5 : 1 and 0.5 : 1. The polymer was found to contain the same amount of Cl_2 (about 40%) between the ratio 1 : 1 and 4 : 1 at constant Cl_2 supply. With increasing ratio, however, the amount of directly bound Cl_2 increases, and that of the chlorine bound as SO_2Cl decreases: the S content drops from 6.34 to 3.24. Experimental series B:

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Sulfochlorination of polypropylene 25261

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Constant SO_2 supply (1 l/hr), and variation of the Cl_2 amount applied. It was found that with increasing ratio Cl_2 : SO_2, the chlorine content in the polymer increases from 21 to 49.16%, the S content drops from 5.71 to 1.57%. Polymers with different Cl_2 and S contents may thus be prepared by changing the ratio. 3) Effect of the amount of the sulfochlorinating agent. The Cl_2 supply was varied between 0.45 - 3 l/g polymer at a molar ratio Cl_2 : SO_2 = 3 : 1. The S content was found to remain constant, while the Cl_2 content dropped from 47 to 40%. The reaction time, however, was at low gas supply 3 hr, at high gas supply 30 min. 4) Effect of reaction time. The experiments were performed with a ratio Cl_2 : SO_2 = 3 : 1, rate of Cl_2 supply 3 l/hr. A table shows the results. Only a part of the gases reacts. A maximum was observed which is explained by saturation of CCl_4 with Cl_2 and SO_2. 5) Properties of the sulfochlorinated polymers: a) the intrinsic viscosity is less than in chlorinated PP with equal Cl_2 content, and depends on the S content. By

Card 3/6

increasing the S content from 2.9 to 6.3%, the intrinsic viscosity decreases from 0.35 to 0.05. A C-C bond separation is assumed which causes a decrease of the molecular weight of the polymer. But no direct proof is available for this assumption. b) The thermomechanical properties show that the temperature of the viscous flow rises by about 70°C with increasing S.content, but that the vitrification temperature remains unchanged. Reduction of the Cl_2 and S content to 1/10 does not affect the thermomechanical properties. The polymer with 1-2% S discloses a range of high elasticity which is limited on one hand by the vitrification temperature, on the other hand by the temperature at which cross linking occurs. When the S content is increased to 5% cross linking immediately follows the viscous flow. If the Cl_2 content is kept constant (about 37%), and if the S content is changed between 0 and 6%, the following will be obtained: a) either a crystalline product in a temperature range between brittleness temperature and softening point, or, b) rubber with a highly elastic state between 150-190°C, or c) solid material with network. There are 6 figures, 1 table, and 7 references: 3 Soviet-bloc and 4 non-Soviet-bloc.

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Sulfochlorination of polypropylene 25261

S/190/61/003/007/005/021
B101/B208

ASSOCIATION: Institut neftekhimicheskogo sinteza AN SSSR (Institute of Petrochemical Synthesis, AS USSR)

SUBMITTED: August 24, 1960

Card 5/6

KRENTSEL', B.A.

Problems involved in the production and study of the properties of polyolefins. Plast.massy no.9:3-10 '61. (MIRA 14:9)
(Olefins)

TOPCIEV, A. V. [Topchiyev, A. B.]; KRENTEL, B. A. [Krentsel', B. A.]; STOTKAIA, L. L. [Stotskaya, L. L.]

Complex organometallic compounds, catalysts of olefin polymerization. Analele chimie 16 no.4:64-99 O-D '61.

(Organic compounds) (Olefins) (Catalysts) (Polymers and polymerization)

TOPCHIYEV, A.V.; KRENTSEL', B.A.; STOTSKAYA, L.L.

Complex organometallic compounds as catalysts in the polymerization of olefins. Usp. khim. 30 no. 4:462-492 Ap '61. (MIRA 14:4)

1. Institut neftekhimicheskogo sinteza AN SSSR.
(Olefins) (Catalysts) (Polymerization)

S/020/61/137/004/025/031
B101/B208

5.1190 1209, 1208, 1267

AUTHORS: Dokukina, Ye.S., Roginskiy, S.Z., Corresponding Member AS USSR, Sakharov, M.M., Topchiyev, A.V., Academician, Geyderikh, M.A., Davydov, B.E., and Krentsel', B.A.

TITLE: Catalysis on organic semiconductors obtained by heat treatment of polyacrylonitrile

PERIODICAL: Doklady Akademii nauk SSSR, v. 137, no. 4, 1961, 893- 895

TEXT: It could be assumed on the basis of the bibliography and the generally accepted concept of the catalytic mechanism that organic semiconductors with small forbidden band width and considerable electrical conductivity at room temperature should be active catalysts in redox reactions. Only qualitative data being available so far, it was the purpose of this study to investigate the catalytic activity of polymer semiconductors containing a system of conjugate bonds on redox reactions in the gaseous and vapor phases. The authors have chosen semiconductors from polyacrylonitrile (PAN). Data on preparation and electrical properties of this material are given in Ref. 7 (A.V. Topchiyev, M.A. Geyderikh et al.,

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DAN, 128, 312 (1959)), and have been reported by M.A. Geyderikh at the International Symposium on Macromolecular Chemistry on June 14 - 18, 1960. Two PAN samples were used: PAN-1 to which 0.01% $CuCl_2$ was added prior to heat treatment, and which had a specific surface of 0.06 m^2/g (determined by means of krypton), and PAN-2 without copper admixture and with a specific surface of 0.04 m^2/g. Catalytic activity was studied in an apparatus similar to that of O.M. Schwab, M. Theophilides (Ref. 13, see below). The catalysts were annealed at 450°C for 1-3 hr prior to the experiment. Considerable catalytic activity was only observed in the decomposition of formic acid. Experimental data are given in Table 1. The copper admixture was found to be of minor importance. As the change of the decomposition rate v of HCOOH was determined by the continuous method on a stepwise rise of temperature, a constant rate of acid addition, and a low degree of conversion (1 - 10%), the activation energy could be calculated from log v = - f(1/T). It was 21 kcal for PAN-1, and 25 kcal for PAN-2. The catalytic activity of the samples increased from experiment to experiment until it reached a constant value. Activation energy, however, remained nearly constant. A catalytic action of PAN on the decomposition of hydrazine hydrate

in NH_3 and N_2 was observed only at high temperatures (250°C) at which the reaction on the glass surface of the vessel and homogeneous decomposition play an important role. The specific activity of PAN with respect to the decomposition of HCOOH is explained by its chemical structure. The N-atoms in the chain of the conjugate bonds are assumed to act as adsorption centers for the acid molecules. By changing the chemical and electrophysical properties of polymers with conjugate double bonds, highly selective catalysts should be obtained which are comparable to those used in fermentative catalysis. This is the reproduction of a report delivered by S.Z. Roginskiy, Corresponding Member AS USSR, before the Uchenyy Sovet Instituta khimicheskoy fiziki Akademii nauk SSSR (Scientific Council of the Institute of Chemical Physics of the Academy of Sciences USSR) on May 27, 1960. Mention is made of A.A. Berlin, L.A. Blyumenfel'd, N.N. Semenov. (Ref. 11: Izv. AN SSSR, OKhN, 1959, no. 9, 1689). There are 1 figure, 2 tables, and 14 references: 8 Soviet-bloc and 6 non-Soviet-bloc. The 3 references to English language publications read as follows: K. Tamaru, T. Shimada, Bull. Chem. Soc. Japan, 31, 141, (1958); D.D. Eley, Res. appl. Ind. 12, 293 (1959); G.M. Schwab, E.

Card 3/5

B1500
S/020/61/137/004/025/031
B101/B208

Catalysis on organic...

Theophilidas, J. phys. Chem., 50, 427 (1946).

ASSOCIATIONS: Institut fizicheskoy khimii Akademii nauk SSSR (Institute of Physical Chemistry, Academy of Sciences USSR), Institut neftekhimicheskogo sinteza Akademii nauk SSSR (Institute of Petrochemical Synthesis of the Academy of Sciences USSR)

SUBMITTED: December 24, 1960

Card 1/3

15.8063

28734
S/020/61/140/003/015/020
B103/B101

AUTHORS: Topchiyev, A. V., Academician, Krentsel', B. A., Dal', V. V., and Oppengeym, V. D.

TITLE: Polymerization of heptene-1 by means of the catalytic system $Al(iso\text{-}C_4H_9)_3 + TiCl_4$

PERIODICAL: Akademiya nauk SSSR. Doklady, v. 140, no. 3, 1961, 614-616

TEXT: The authors studied the mechanism of polymerization of linear α- olefins by combined organometallic catalysts, as well as the relations between the structure of the initial hydrocarbon and the properties of the resulting polymer. Heptene-1 served as object, $Al(i\text{-}C_4H_9)_3 + TiCl_4$ as catalyst. The monomer was prepared by pyrolysis of heptyl acetate at 540 - 550°C. Preliminary tests showed that the highest conversion of the monomer was reached at an equimolar quantitative ratio of the catalyst components, and at approximately 60°C. The course of temperature of the intrinsic viscosity of polyheptene revealed: Above 60°C some destruction of the polymer set in under the action of the catalyst. As a result, the

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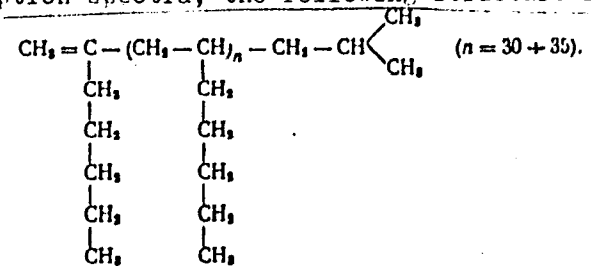
28734
S/020/61/140/003/015/020
B103/B101

Polymerization of heptene-1...

intrinsic viscosity which depends on the ratio of the catalyst components dropped. The peak value of the intrinsic viscosity in Decalin was reached at an $AlR_3/TiCl_4$ ratio between 1.5 and 2.5. The polyheptene produced under optimum conditions is a viscous, glassy substance with a molecular weight of approximately 3500, and a melting point of -40°C. An X-ray structural analysis showed that polyheptene was completely amorphous. On account of the infrared absorption spectra, the following structure is assumed:

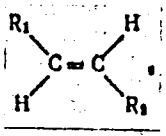


$(n = 30 + 35)$.

Still, the absorption band at 972 cm^{-1} points to a possible double bond in the middle of the polymer chain:

Card 2/3

Polymerization of heptene-1...



This problem requires further investigation. There are 3 figures and 4 references: 1 Soviet and 3 non-Soviet. The three references to English language publications read as follows: F. P. Reding, J. Polym. Sci., 21, 547 (1956); E. Badin, J. Am. Chem. Soc., 80, 24 (1958); T. W. Campbell, A. C. Haven jr., J. Appl. Polym. Sci., 1, No. 1 (1959).

ASSOCIATION: Institut neftekhimicheskogo sinteza Akademii nauk SSSR (Institute of Petrochemical Synthesis of the Academy of Sciences USSR)

SUBMITTED: May 29, 1961

Card 3/3

BAKALO, L.A.; KRENTSEL', B.A.; PYRKOV, L.M.; TOPCHIYEV, A.V., akademik; FRENKEL', S.Ya.

Mechanism of epichlorohydrin polymerization on the catalytic system $FeCl_3$ X propylene oxide. Dokl. AN SSSR 141 no.3:613-615 N '61. (MIRA 14:11)

1. Institut neftekhimicheskogo sinteza AN SSSR.
(Epichlorohydrin) (Polymerization)

KRENTSEL', Boris Abramovich; ROKHLIN, Maks Isaakovich; TARASENKO, V.M., red. izd-va; POLYAKOVA, T.V., tekhn. red.

[New chemistry and its raw material resources] Novaia khimiia i ee syr'evaia baza. Moskva, Izd-vo Akad. nauk SSSR, 1962. 103 p. (MIRA 15:7)
(Chemistry, Technical)

43244

S/844/62/000/000/105/129
D204/D307

AUTHORS: Gulyayev, G. V., Davydov, B. E., Krentsel', B. A., Patalakh, I. I. and Polak L. S.

TITLE: The effect of radiation on semiconducting polymeric materials

SOURCE: Trudy II Vsesoyuznogo soveshchaniya po radiatsionnoy khimii. Ed. by L. S. Polak. Moscow, Izd-vo AN SSSR, 1962, 621-624

TEXT: The effects of γ and electron irradiation on polymers based on polyacrylonitrile (PAN) were studied, to determine the nature of such materials. The (powdered) specimens were prepared by catalytic or radiational polymerization; a polyacrylonitrile fabric was also tested. The specific electron conductance (σ, 10^{-10} $ohms^{-1}.cm^{-1}$) of hot-pressed (15,000 atm, 350°C) radiation polymerized PAN was lower than that of catalytically polymerized PAN (~2.6 - 3.6) and decreased, by a factor of 10 - 15, with increasing power of the dose used to induce polymerization (10^6 r, the latter were varied from 23

Card 1/2

to 140 r/sec.cm^3, at 25^{0}C). The σ of catalytic PAN polymerized at 28 r/sec.cm^3, increased on irradiation with increasing doses, up to ~10 and ~5 respectively at 5 Mr; further increase was only slight. The σ of PAN polymerized at 75 and at 140 r/sec.cm^3 was unaffected by irradiation. The energy of activation (= 0.4 ev) remained constant in all cases. The specific conductance of PAN fabric increased on irradiation, from ~10^{-5} at 0 to ~10^{-3} ohm^{-1}cm^{-1} at 140 Mr, whilst the energy of activation fell from 0.33 to 0.2 ev. Similar effects were observed by subjecting the fabric to 0.7 Mev electrons. The various changes observed in these semiconducting polymers on irradiation are ascribed to differences in the macrostructure of the polymer. There are 4 figures.

ASSOCIATION: Institut neftekhimicheskogo sinteza AN SSSR (Institute of Petrochemical Synthesis, AS USSR)

S/191/62/000/012/001/015
B101/B186

AUTHORS: Topchiyev, A. V., Stotskaya, L. L., Krentsel', B. A.

TITLE: Polymerization of ethylene and some other vinyl monomers with soluble catalyst systems

PERIODICAL: Plasticheskiye massy, no. 12, 1962, 3-12

TEXT: This is a review article covering papers published between 1948 and 1962 on the reaction mechanism of the polymerization of ethylene, propylene, isoprene, butadiene and other dienes with soluble Ziegler-Natta-type catalysts. It is pointed out that the reaction medium considerably affects the course of polymerization when soluble metallo-organic complexes are used. From a theoretical aspect, based on the findings of the research it is assumed possible to simulate biological processes with the aid of soluble organic catalysts. There are 2 figures, 11 tables, and 44 references.

Card 1/1

S/064/62/000/012/002/006
B119/B180

AUTHORS: Krentsel', B. A., Doctor of Chemical Sciences

TITLE: Stereoregular polymers

PERIODICAL: Khimicheskaya promyshlennost', no. 12, 1962, 6 - 12

TEXT: The article reviews Western and Soviet research work carried out between 1956 and 1962 on the synthesis of stereoregular polymers. Special attention is paid to polymers with industrial possibilities, e.g. polyhydrocarbons, polyvinyl chloride, and polymers containing oxygen in the principal chain. There are 2 tables and 37 references.

Card 1/1

KRENTSEL', B.A.; SIDOROVA, L.G.; SHISHKINA, M.V.; KUSAKOV, M.M.; KORENEVSKAYA, F.V.; SHCHEKIN, V.V..

Conversion polymerization of α-olefins. Neftekhimiia 2 no.5: 705-708 S-O '62. (MIRA 16:1)

1. Institut neftekhimicheskogo sinteza AN SSSR.
(Olefins) (Polymerization)

S/190/62/004/012/004/015
B101/B186

AUTHORS: Yerasova, Ye. L., Krentsel', B. A., Pokatilo, N. A., Topchiyev, A. V.

TITLE: Isomerizing action of the catalytic system $Al(C_2H_5)_3$ + $CrCl_3$ in the polymerization of but-1-ene

PERIODICAL: Vysokomolekulyarnyye soyedineniya, v. 4, no. 12, 1962, 1796-1798

TEXT: The applicability of the catalyst $Al(C_2H_5)_3$ + $CrCl_3$ suggested by J. E. Gillespie, J. W. Tordman (Industr. and Engng. Chem., 51, 1365, 1959) for the polymerization of propylene was studied with respect to the polymerization of but-1-ene. The experiments were carried out in ampoules, with the ratios $Al(C_2H_5)_3$: $CrCl_3$ = 1:1, 1:2, 1:6, and 1:9 at 30-80°C. The polybutene yield was only 5%. However, a considerable isomerization from 1-butene to 2-butene was observed, which did not occur in the polymerization of 1-butene with AlR_3 + $TiCl_4$. Example: The initial butene had the composition (in % by weight): 70.03 1-butene, 11.42 cis-2-butene, and

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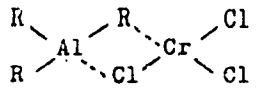
Isomerizing action of the...

18.55 trans-2-butene. After 30 hrs action of a catalyst with the ratio $(C_2H_5)_3Al$: $CrCl_3$ = 4:1 at 80°C, the composition was 24.41 1-butene, 41.07 cis-2-butene, and 34.52 trans-2-butene. Since $CrCl_3$ alone showed nearly no isomerizing effect, this is ascribed to the catalyst complex



There is 1 table.

ASSOCIATION: Institut neftekhimicheskogo sinteza AN SSSR (Institute of Petrochemical Synthesis AS USSR)

SUBMITTED: July 1, 1961

BAKALO, L.A.; KRENTSEL', B.A.

Catalytic polymerization of organic α-oxides. Usp.khim. 31 no.6:657-669 Je '62. (MIRA 15:5)

1. Institut neftekhimicheskogo sinteza AN SSSR.
(Ethylene oxide) (Polymerization)

KRENTSEL', B.A., doktor khim.nauk

Conference on ionic polymerization. Vest.AN SSSR 32 no.4:103-104 Ap '62. (MIRA 15:5)

(Polymerization—Congresses)

KRENTSEL', B.A., doktor khim.nauk

Exhibition of synthetic materials in Paris. Vest. AN SSSR 32 no.11:114-117 N '62. (MIRA 15:11)
(Synthetic products--Exhibitions)
(Paris--Exhibitions)

32837

S/020/62/142/002/018/029
B106/B101

51190 1407

AUTHORS: Bakalo, L. A., Krentsel', B. A., Oppengeym, V. D., and Topchiyev, A. V., Academician

TITLE: The structure of the $FeCl_3$/propylene oxide catalyst and the mechanism of stereospecific polymerization of some epoxy compounds

PERIODICAL: Akademiya nauk SSSR. Doklady, v. 142. no. 2, 1962, 347-350

TEXT: The polymerization of organic oxides on a catalyst from anhydrous ferric chloride and propylene oxide takes a stereospecific course which is usually attributed to the heterogeneity of the catalytic system (Ref. 3: C. C. Price, M. Osgan, J. Am. Chem. Soc., 78, 4789 (1956)). In a previous study (Ref. 6: L. A. Bakalo, B. A. Krentsel', A. V. Topchiyev, Vysokomolek. soyed. 4 (1962)), however, the authors found that the polymerization of epichlorohydrin and divinyl monoxide on the catalyst mentioned also takes a stereospecific course, although the system monomer - catalyst is perfectly homogeneous. The structure of the catalyst has now been

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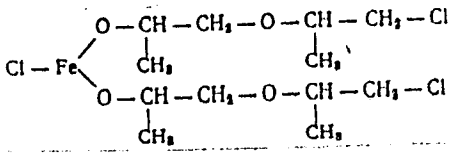
The structure of the $FeCl_3$/propylene...

investigated to clarify the mechanism of stereospecific polymerization. The catalyst was prepared, according to Ref. 2 (see below), from sublimed $FeCl_3$ and propylene oxide in dry CCl_4. Its composition in % was: Fe 15.06; C 37.33; H 6.56; Cl 21.26. To seperate the organic part, the catalyst was dissolved in acetone, and the iron was precipitated with sodium hydroxide. The resulting suspension was diluted with water and extracted with ether. The extract was rinsed with water, soda solution, and again with water, and dried over Na_2SO_4. After evaporating the ether, the residue was fractionated (20 - 30 theoretical plates)in a vacuum of 1.5 mm Hg. Three fractions (b. p. 45.5 - 46.5°C, 46.5 - 47.5°C, and 47.5 - 49.0°C, respectively) were collected and subjected to elementary analysis, as was the residue. The molecular weight of the catalyst was determined according to Rast, and the content of mobile hydrogen in the organic portion of the catalyst according to Tserevitinov, with ethyl magnesium iodide. It has been proved by nephrite-test and on the basis of infrared spectra that the organic portion contains chlorine. Thus, the empirical molecular formula of the catalyst was found to be $ClFe(C_6H_{12}O_2Cl)_2$. The structure of the organic portion of the catalyst was

Card 2/4

The structure of the $FeCl_3$/propylene...

clarified by infrared spectroscopy (UKS-14 (IKS-14) spectrophotometer in the frequency range of 1800 - 640 cm^{-1}). In this connection, the arrangement of the epoxy ring opening with subsequent development of the ether bond was ascertained. It has been proved that the opening of the epoxy ring during the reaction of ferric chloride with propylene oxide takes place at the primary carbon atom, the configuration at the secondary carbon atom being maintained. These results provided the following structural formula for the catalyst in question:



It is of interest that also the organic portion of the catalyst from anhydrous ferric chloride and epichlorohydrin shows the same arrangement of ether bonds. This result and the previously (Ref. 6) shown homogeneous character of the system indicate that the opening of the oxygen-containing ring at the primary carbon atom, in which the configuration at the

asymmetric carbon atom during polymerization is maintained, is the cause for the stereospecificity of polymerization of the α-oxides of olefins. Previous orientation of the monomer, as assumed by Price and collaborators (Ref. 3), is therefore not required in this case. There are 1 figure, 1 table, and 8 references: 2 Soviet and 6 non-Soviet. The four most recent references to English-language publications read as follows: Ref. 2: A. B. Borkovec, US pat. 2861962 (1958); R. O. Colclough, G. Gee, W. C. E. Higginson et al., J. Polymer Sci., 34, 171 (1959); I. Ishida, Bull. Chem. Soc., Japan, 33, 731 (1960); S. Misushima, T. Shimanouchi et al., J. Chem. Phys., 26, 970 (1957).

ASSOCIATION: Institut neftekhimicheskogo sinteza Akademii nauk SSSR (Institute of Petrochemical Synthesis of the Academy of Sciences USSR)

SUBMITTED: October 6, 1961

15.8060

S/020/62/146/002/010/013
B101/B144

AUTHORS: Stotskaya, L. L., Topchiyev, A. V., Academician, Krentsel', B. A.

TITLE: Polymerization of ethylene with the soluble, complex, organometallic catalyst $Sn(C_6H_5)_4 + AlCl_3 + VCl_4$

PERIODICAL: Akademiya nauk SSSR. Doklady, v. 146, no. 2, 1962, 372-375

TEXT: C_2H_4 was polymerized using this catalyst suggested by W. L. Carrick et al. (J. Am. Chem. Soc., 82, 3883 (1960)) at 65°C and under atmospheric pressure, in order to obtain polyethylene free of catalyst impurities giving a high specific polymer yield per unit weight of catalyst, and close molecular-weight distribution. The reaction vessel was filled with cyclohexane, tetraphenyl tin was added, and the solution was saturated with C_2H_4. Then a cyclohexane solution of VCl_4 and a solution of $AlCl_3$ saturated in hot cyclohexane were added dropwise, and C_2H_4 was bubbled through the solution. After one hour the polymer was precipitated with methanol. Results: The amounts of polymer obtained per gram catalyst

Polymerization of ethylene...

were: 12.8, 16.2 and 19.8 %, respectively, with 0.165 mmoles $Sn(C_6H_5)_4$, 0.01 mmoles VCl_4, and 0.26, 0.38, or 0.45 mmoles $AlCl_3$. The intrinsic viscosities of the polymers in decahydronaphthalene at 120°C were 2.5, 3.2, and 4.1, respectively. The sequence in which the catalyst components were added did not affect the polymerization. The low specific yield is explained by the complete absence of oxygen. The effect of a small oxygen content (G. A. Phillips, N. L. Carrick, Papers presented at the 3[illegible] Meeting, March 1, no. 2, 1961, p. 56) is explained by higher vanadium valences with the complex catalyst acting as redox system. The IR spectrum proved the presence of polyethylene links (1456, 1297, 722, 709 cm^{-1}) and the absence of olefin and CH_3 groups. An x-ray analysis confirmed the high crystallinity of the polymer, and a thermomechanical examination showed a region of high elasticity between 200 and 300°C with a yield point >300°C. At 80°C, the relative elongation was <700%. Polyethylene showed a high molecular weight and a linear structure similar to polymethylene. Further data will be published relating to an investigation of polymerization processes with the Mössbauer effect. There are 2 figures and 1 table.

Card 2/3

S/020/62/146/002/010/013
Polymerization of ethylene... B101/B144

AUTHORS: Institut neftekhimicheskogo sinteza Akademii nauk SSSR (Institute of Petrochemical Synthesis of the Academy of Sciences USSR)

PERIOD: May 29, 1962

Card 3/3

TOPCHIYEV, A.V., akademik; KORSHAK, Yu.V.; DAVYDOV, B.E.; KRENTSEL', B.A.

Polyazines, a new class of polymers with conjugate bonds. Dokl. AN SSSR 147 no.3:645-648 N '62. (MIRA 15:12)

1. Institut neftekhimicheskogo sinteza AN SSSR.
(Azines) (Polymers) (Conjugation (Chemistry))

SEMENIDO, G. Ye.; IL'INA, D. Ye.; SHISHKINA, M. V.; KRENTSEL', B. A.

Polymerization of trichloroacetaldehyde in the presence of an organometallic catalyst. Dokl. AN SSSR 147 no.6:1386-1388 D '62. (MIRA 16:1)

1. Institut neftekhimicheskogo sinteza AN SSSR. Predstavleno akademikom A. V. Topchiyevym.

(Acetaldehyde) (Polymerization)
(Catalysts)

BAKALO, L.A.; KRENTSEL', B.A.; TOPCHIYEV, A.V.

Polymerization of some organic oxides. Part 1: Polymerization of epichlorhydrin. Vysokom.soed. 4 no.9:1361-1365 S '62. (MIRA 15:11)

1. Institut neftekhimicheskogo sinteza AN SSSR.
(Epichlorhydrin) (Polymerization)

TOPCHIYEV, A.V.; STOTSKAYA, L.L.; KRENTSEL', B.A.

Polymerization of ethylene and some other vinyl monomers with soluble catalytic systems. Plast. massy no.12:3-12 '62.
(MIRA 16:1)

(Ethylene) (Polymerization) (Catalysts)

KRENTSEL', B.A., doktor khimicheskikh nauk

Stereoregular polymers. Khim.prom. no.12:864-870 D '62.
(MIRA 16:2)

(Macromolecular compounds)

YERASOVA, Ye.L.; KRENTSEL', B.A.; POKATILO, N.A.; TOPCHIYEV, A.V.

Isomerizing action of the catalytic system $Al(C_2H_5)_3+CrCl_3$ in the polymerization of 1-butene. Vysokom. soed. 4 no.12:1796-1798 D '62. (MIRA 15:12)

1. Institut neftekhimicheskogo sinteza AN SSSR.
(Butene) (Polymerization) (Catalysts)

TOPCHIYEV, Aleksandr Vasil'yevich, akademik; KRENTSEL', Boris Abramovich, doktor khim. nauk; TARASENKO, V.M., red. izd-va; VOLKOVA, V.V., tekhn. red.

[Polyolefins are the new synthetic materials] Poliolefiny - novye sinteticheskie materialy. Izd.2., perer. i dop. Moskva, Izd-vo AN SSSR, 1963. 93 p. (MIRA 17:1)

STIL'BANS, L.S., doktor fiz.-mat. nauk; ROZENSHTEYN, L.D., kand. fiz.-mat. nauk; AYRAPETYANTS, A.V., kand. fiz.-mat. nauk; KARGIN, V.A., akademik; KRENTSEL', B.A., doktor khim. nauk; TOPCHIYEV, A.V., akademik [deceased]; DAVYDOV, B.E., kandid.khim. nauk; GEVSEN, L.V., red.; MIYESSEROV, K.G., red.; GOLUB', S.P., tekhn. red.

[Organic semiconductors] Organicheskie poluprovodniki. Moskva, Izd-vo AN SSSR, 1963. 317 p. (MIRA 16:12)

1. Akademiya nauk SSSR. Institut neftekhimicheskogo sinteza.
(Semiconductors)

KRENTSELM B.A., SIDOROVA, L.G., TOPICHEV, A.V., (Deceased)

Principles of conversational polymerization of unsaturated hydrocarbons.

Report submitted for the International Symposium of Macromolecular Chemistry, Paris, 1-6 July 63

ILINA, D.YE., KMENTSEL, B.A., SEMENIDO, YE.G.

Low-temperature polymerization of chlorine-substituted aldehydes.

Report submitted for the International Symposium of Macromolecular chemistry, Paris, 1-6 July 63

AYRAPETYANTS, A.V., VOYTENKO, R.M., DAVYDOV, B.E. KRENTSEL, B.A.

Conductance mechanism in organic semi-conductor polymers

Report submitted for the International Symposium of Macromolecular chemistry
Paris, 1.6 July 63

KRENTSEL', B.A.; IL'INA, D.Ye.; ADYLOV, S.A.

Chlorination and sulfochlorination of polyolefins. Plast. massy no.6:3-8 '63. (MIRA 16:10)

POPOV, Yu.A.; DAVYDOV, B.E.; SHISHKINA, M.V.; KRENTSEL', B.A.

Thermal conversions of polymeric Schiff bases. Izv. AN SSSR. Ser. khim. no.11:2014-2019 N '63. (MIRA 17:1)

1. Institut neftekhimicheskogo sinteza AN SSSR.

ADYLOV, S.A.; LESHCHEVA, I.F.; IL'INA, D.Ye.; SHISHKINA, M.V.; KRENTSEL', B.A.

Chemical structure of some chlorinated polyolefins. Neftekhimiia 3 no.1:82-89 Ja-F '63. (MIRA 16:2)

1. Institut neftekhimicheskogo sinteza AN SSSR.
(Olefins) (Chlorination)
(Chemical structure)

BAKALO, L.A.; KRENTSEL', B.A.; TOPCHIYEV, A.V. [deceased]

Catalytic polymerization of epichlorohydrin. Neftekhimiia 3 no.2: 206-216 Mr-Ap '63. (MIRA 16:5)

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(Epichlohydrin) (Polymerization)

S/190/63/005/003/003/024
B101/B186

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TITLE: Interaction of chlorinated polyethylene with amines and ammonia

PERIODICAL: Vysokomolekulyarnyye soyedineniya, v. 5, no. 3, 1963, 316-320

TEXT: A study was made of the reaction of chlorinated polyethylene suspended in toluene with aniline or di-n-butylamine at 50 - 70°C, as well as of the reaction of chlorinated polyethylene with aqueous ammonia solution in glass ampuls in nitrogen atmosphere at 70°C. The chlorination of the high-density polyethylene (m.p. 132°C, $[\eta]$ = 4.15 in decalin at 135°C) was made according to a method devised for the chlorination of polypropylene (Zh. prikl. khimii, 32, 1404, 1959). Results: the IR spectra of the chlorinated polyethylene showed the presence of C-Cl bonds. Chlorinated products of different chlorine content were obtained. The intrinsic viscosity decreased as the chlorine content increased. It was 4.1 at 1.3% Cl and 0.7 at 60.9% Cl. X-ray analysis showed that the crystalline structures